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14. ABSTRACT
A significant amount of research was accomplished in the design, development, characterization and applications of two types of photonic materials: Multiphoton absorbing materials and hybrid nanocomposites for photorefractivity. We synthesized a new class of two-photon dyes which are pyridinum-based inner salts (covalently bonded) and achieved two-photon lasing. Another accomplishment was to produce two-photon active liquid dyes with enhanced number density. In collaboration with AFRL at Dayton who synthesized 1,3,5 triazine-based octupolar molecules, we characterized their two-photon properties using our newly developed femtosecond white light continuum transient absorption method. This method was also utilized to characterize the two-photon absorption spectrum of a series of highly two-photon active chromophores synthesized by the AFRL at Dayton. We also successfully synthesized a number of highly efficient three-photon materials.

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Inorganic Quantum Dots, Transporting Polymeric Medium, Liquid Crystal Nanocomposite Photosensitized with Quantum Dots.

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Final Report
05/01/04

Prime Contract: F49620-03-1-0103

**New Generation Photonics Materials: Design, Development,
Characterization and Applications**

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SUMMARY OF ACCOMPLISHMENTS

A significant amount of research was accomplished in the design, development, characterization and applications of two types of photonic materials: Multiphoton absorbing materials and hybrid nanocomposites for photorefractivity. We synthesized a new class of two-photon dyes which are pyridinum-based inner salts (covalently bonded) and achieved two-photon lasing. Another accomplishment was to produce two-photon active liquid dyes with enhanced number density. In collaboration with AFRL at Dayton who synthesized 1,3,5 triazine-based octupolar molecules, we characterized their two-photon properties using our newly developed femtosecond white light continuum transient absorption method. This method was also utilized to characterize the two-photon absorption spectrum of a series of highly two-photon active chromophores synthesized by the AFRL at Dayton. We also successfully synthesized a number of highly efficient three-photon materials.

A number of new applications of these multiphoton materials were also demonstrated. A holographic polymer-dispersed liquid-crystal grating was demonstrated as a distributed feedback element for tunable two-photon pumped up-conversion lasing. Two-photon fluorescence guided laser tweezers were used to study optical trapping forces and to study cluster growth and gelatin process. The biophotonics applications in bioimaging and in up-conversion photodynamic therapy were investigated.

A fundamental understanding of charge carrier mobility is important in order to enhance the response time and efficiency of photorefractivity. We conducted a thorough study of the mobility in a quantum dot:polymer composite and found an unexpected result of enhancement of hole mobility in the polymer, even by adding a small concentration of the quantum dots. This discovery can lead to improved solar devices.

ACCOMPLISHMENTS UNDER CURRENT SUPPORT

A great deal of progress was made in the development of new generation Photonics materials, their characterization and applications. Here only highlights of major accomplishments are presented.

- **Synthesis and Properties of Substituted (p-Aminostyryl)-1-(3-Sulfooxypropyl) Pyridinium Inner Salts as a New Class of Two-Photon Pumped Lasing Dyes[1]**

A series of substituted (p-aminostyryl)-1-(3-sulfooxypropyl)pyridinium (ASSP) inner salts have been synthesized and characterized. For comparison purposes substituted (p-aminostyryl)pyridinium iodide (ASPI) salts and substituted (p-aminostyryl)pyridinium tosylate (ASPT) salts were also prepared. Their linear absorption, two-photon absorption and emission properties have been studied. All these dyes exhibit relatively large two-photon absorption (TPA) cross-section values at 1064 nm wavelength. When pumped by 1064 nm IR laser beam, two-photon pumped (TPP) frequency up-conversion lasing was observed in all these dyes, except for trans-4-{p-[N-methyl-N-(2-acetic acid ethyl ester)amino]styryl}-1-methylpyridinium tosylate. The TPP lasing peaks of these dyes range from 612 nm to 637 nm, with half bandwidths varying from 2 nm to 11 nm. Compared with the substituted ASPI salts or the substituted ASPT salts, the substituted ASSP inner salts show enhanced TPP lasing. The TPP lasing efficiency of trans-4-{p-[N-ethyl-N-(2-hydroxyethyl)amino]styryl}-1-(3-sulfooxypropyl)pyridinium, inner salt is as high as 27%.
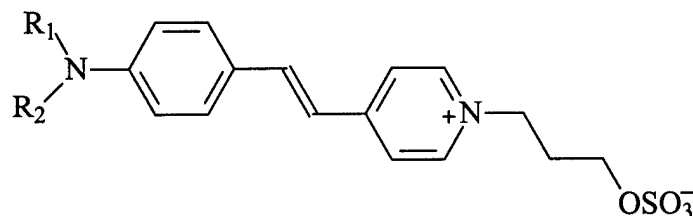

1. Q. Zheng, G. S. He, T.-C. Lin and P. N. Prasad, *J. Mater. Chem.* **13**, 2499-2504 (2003).

- **Toward Highly Active Two-Photon Absorbing Liquids. Synthesis and Characterization of 1,3,5-Triazine-Based Octupolar Molecules[2]**

Three novel two-photon absorbing (TPA) chromophores with 1,3,5-triazine as the π-electron deficient core, dialkylfluorene as aromatic bridges, and diphenylamino groups as the electron-donating end-groups were prepared. Designated as **AF-450** (2,4,6-tris[7-(diphenylamino)-9,9-didecylfluoren-2-yl]-1,3,5-triazine), **AF-455** (2,4,6-tris[9,9-bis(3,7-dimethyloctyl)-7-(diphenylamino)-fluoren-2yl]-1,3,5-triazine), and **AF-457** (2,4,6-tris[(7-(diphenylamino)-9,9-diprop-2-enylfluoren-2-yl]-1,3,5-triazine), their overall molecular

structure and local symmetry (D_{3h}) are similar to those of previously reported three-armed **AF-350** (*N,N,N*-tris[4-{7-(2-benzothiazolyl)-9,9-diethylfluoren-2-yl}phenyl]amine) and **AF-380** (*N,N,N*,-tris[7-(2-benzothiazolyl)-9,9-diethylfluoren-2-yl]amine). Among the family of AFX chromophores previously reported by us, **AF-450** possesses one of the largest *effective* TPA cross-sections ($\sigma_2' = 39\ 500 \times 10^{-50}$ cm^4-sec/photon-molecule, or 39 500 GM) as determined by nonlinear transmission method in the nanosecond regime at 800 nm. In contrast, **AF-455**, a mixture of stereoisomers with the same chemical formula as **AF-450**, is a glassy material that becomes fluid (molasses-like) upon heating at 70-80 °C and has noticeably smaller effective σ_2' value (33 300 GM). **AF-457** ($\sigma_2' = 27\ 800$ GM) with six allyl side groups was prepared as a precursor toward the synthesis of a TPA liquid. The intrinsic TPA cross-sections of these chromophores were also determined as a function of excitation wavelengths via a femtosecond white-light continuum generation and direct degenerate-TPA measurement technique. At the TPA peaks ~779 nm, their σ_2' values are 216, 214, and 199 GM ($\pm15\%$) for **AF-450**, **AF-455**, and **AF-457**, in that order. They are in the same trend as the nanosecond values, albeit two orders of magnitude lower.
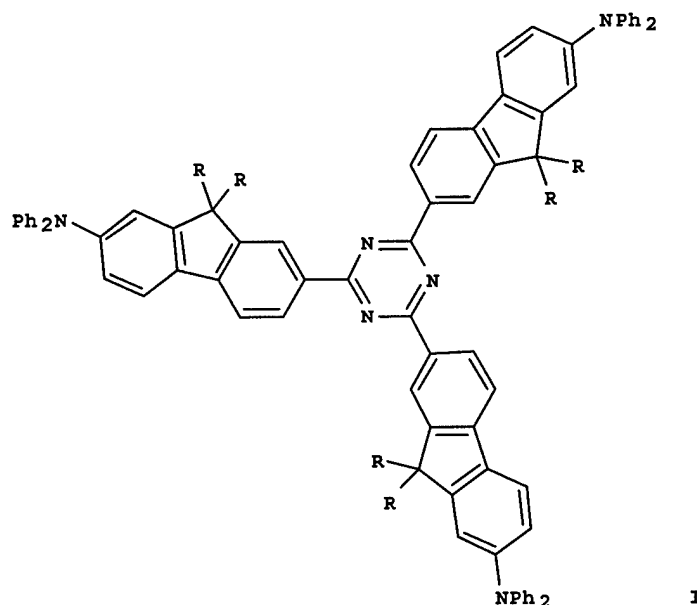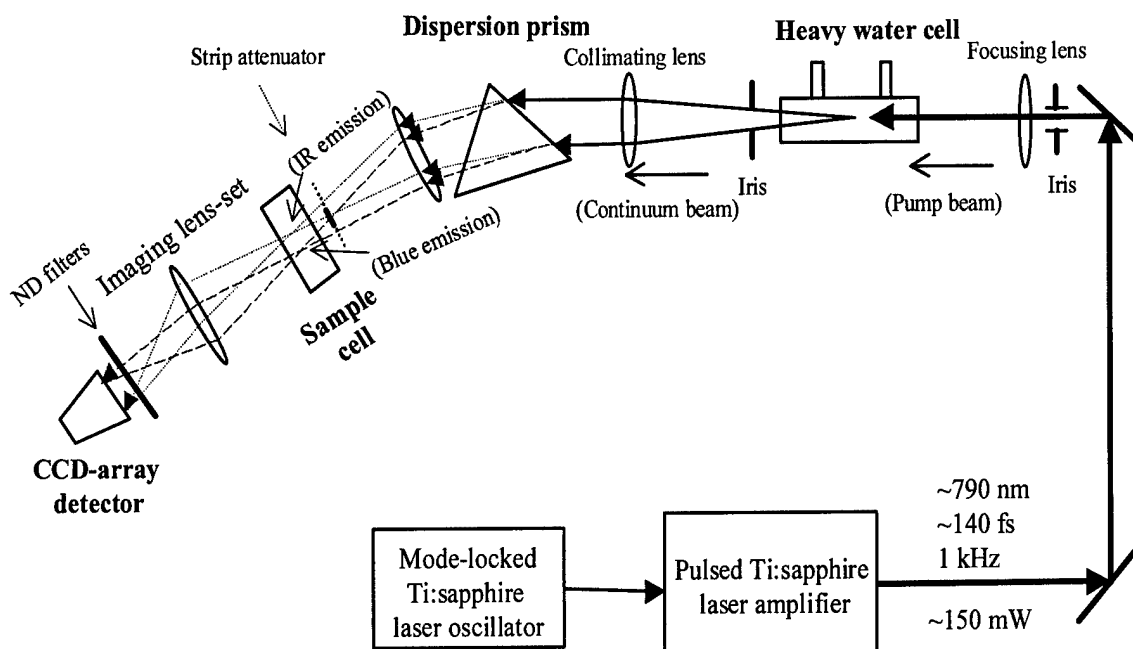

2.R.Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia, and L.-S. Tan, *Chem. Mater.* **16**, 185-194 (2004).

- **Degenerate Two-Photon Absorption Spectral Studies of Highly Two-Photon Active Organic Chromophores**[3]

Degenerate two-photon absorption (TPA) spectral properties of five AFX chromophore solutions have been studied using a single and spectrally dispersed sub-picosecond white-light continuum beam. In a specially designed optical configuration, optical pathways inside the sample solution for different spectral components of the focused continuum beam were spatially separated from each other. Thus, the non-degenerate TPA processes coming from different spectral components can be eliminated,

and the direct nonlinear absorption spectrum attributed to degenerate TPA processes can be readily obtained. Using this new technique, the complete TPA spectra for these five highly two-photon-active compounds (AF-380, AF-350, AF-295, AF-270, and AF-50) were obtained in the spectral range from 600- to 950-nm on an absolute scale of TPA cross-section. The relationship between the molecular structures and their TPA spectral behaviors are discussed. In general the measured TPA spectra are not identical with the linear absorption spectra on the scale of absorbed photon(s) energy. Moreover, for some sample (such as AF-380), the TPA spectrum is totally different from the linear spectrum, which implies the difference of molecular transition pathways and selection rules for one- and two-photon excitation processes. At high excitation intensity levels ($\geq$15 GW/cm^2), the saturation behavior of TPA transition can be observed obviously in AF-350 and AF380 solutions that exhibit much higher nonlinear absorptivity than the other chromophores investigated.

3. G. S. He, T.-C. Lin, J. Dai, P.N. Prasad, R. Kannan, A. G. Dombroskie, R. A. Vaia and L.-S. Tan, *J. Chem. Phys.* **120**, 5275-5284 (2004).

- **Three-Photon Absorbing Materials: Characterization and Applications[4]**

Recent successes in developing two-photon absorption (2PA) materials and applications have now created significant interest in exploring three-photon absorption (3PA) based novel optical materials and new applications. 3PA-based techniques may exhibit two major advantages: (1) much longer IR wavelengths (1.2-1.7 μm) can be used, and (2) much better beam confinement (resolution) can be achieved owing to the cubic dependence of nonlinear absorption on the local intensity of the excitation IR light. We

have demonstrated efficient three-photon excitation in a number of nonlinear organic materials developed at our Institute. Applications of novel and highly efficient three-photon absorbing materials include (i) three-photon pumped (3PP) and frequency upconverted lasing, (ii) 3PA-based optical power limiting and stabilization, (iii) 3PA-based bio-imaging via IR to visible conversion, and (iv) 3PA-associated 3D data storage and microfabrication. Some recent experimental results of 3PP lasing as well as 3PA-based power limiting are briefly presented.

4. G. S. He and P. N. Prasad, *SPIE Proceedings*, **5211**, 1-11 (2003).

- **Tunable Two-Photon Pumped Lasing Using a Holographic Polymer-Dispersed Liquid-Crystal Grating as a Distributed Feedback Element[5]**

A holographic polymer-dispersed liquid-crystal (H-PDLC) grating film was employed as an angle-dependent and narrow spectral-band feedback control element for two-photon pumped lasing in a dye solution (APSS in DMSO). The grating film contained about 80 layers of liquid-crystal domains periodically dispersed in an ~15 μm thick polymer film, featuring a maximum reflectance of 75% at 561-nm position with an ~9-nm spectral bandwidth. The output lasing wavelength could be tuned from 561.5 to 548.5 nm and the lasing bandwidth changed from 5 to 3 nm when the incidence angle on the grating film varied from 0° to 22°. The overall lasing efficiency was measured to be 10%.

5. G. S. He, T.-C. Lin, V. K. S. Hsiaso, A. N. Cartwright and P.N. Prasad, *Appl. Phys. Lett.* **83**, 2733-2735 (2003).

- **Measurement of Optical Trapping Forces using Two-photon Excited Fluorescence of Microspheres[6]**

A novel technique for the calibration of laser trapping systems that utilizes two-photon excited fluorescence of commercial dye stained microspheres has been demonstrated. The trapping forces as well as the trapping efficiency have been measured for varying liquid environments and trapping depths. The trapping efficiency in water was found to decrease with an increase of trapping depths due to the enlargement of the trapping beam waist caused by aberrations of the optical system.

6. A.V. Kachynski, A.N. Kuzmin, H.E Pudavar, D.S. Kaputa, A.N. Cartwright, P.N. Prasad, Opt Lett. <u>28</u>, 2288-2290 (2003)

- **Two-Photon Fluorescence Guided Laser Tweezers for Study of Cluster Growth and Gelation Process[7]**

Laser tweezer trapping technology has been used to monitor the bulk solution viscosity during the sol-gel gelation process at different depths from an interface. The gelation rate is the same in depth ranges 2 - 20 microns from the bounding surface. Simultaneously with the laser tweezer study, a micro-viscosity kinetic measurement of the sol-gel process was performed by two-photon excited fluorescence anisotropy and quantum yield methods. The large differences found between the bulk and micro-viscosities obtained in the experiment reflect the intrinsic differences in solution environment sensed by the laser tweezer on the macro-level and by other optical techniques on the micro- levels.

7. A.N. Kuzmin, A.V. Kachynski, T.Y. Ohulchanskyy, I. Roy, P.N. Prasad, S. Bruckenstein, Appl. Phys. Lett. <u>84</u>, 2454-2456 (2004).

- **Biophotonics: An Exciting Frontier[8]**

Biophotonics, which involves the integration of four major technologies: lasers, photonics, nanotechnology and biotechnology, offers a new dimension for development of new diagnostic and therapeutic approaches. This workcovers two focus areas of biophotonics, optical bioimaging and light activated photodynamic therapy. It also introduces novel applications of nanotechnology to bioimaging and drug delivery.
Principles of few bioimaging techniques and some examples of bioimaging at the microbial, cellular and tissue level was presented. Nonlinear optical processes, specifically multiphoton absorption, in bioimaging and photodynamic therapy was also discussed. The novel applications of nanotechnology to bioimaging and drug delivery was introduced.

8. H.E. Pudavar, T.Y. Ohulchanskyy, E.J. Bergey, and P.N. Prasad, Nonlinear Optics, Quantum Optics <u>30</u>, 115-147 (2003).

- **Charge Carrier Transport in Poly(N-vinylcarbazole):CdS Quantum Dot Hybrid Nanocomposite[9]**

Hybrid organic:inorganic materials have emerged as a novel class of electronic and optoelectronic media for a number of potential technological applications. Knowledge of the influence of nanoparticle doping on charge carrier mobility in nano

composites becomes important in order to optimize properties for photorefractive and photovoltaic operations. We have done a study of the mobility of holes in a model nanoparticle-sensitized hybrid organic:inorganic system consisting of poly(N-vinylcarbazole) (PVK) doped with quantum dots of cadmium sulfide. The mobility of holes (dominant carriers in the PVK host materials) was measured using the conventional time-of-flight technique with injection of holes from a selenium layer. Photocurrent transients exhibit features typical of dispersive transport in an amorphous semiconductor, but deviations from the original Scher-Montroll theory are observed. This is attributed to the fact that measurements have been performed under conditions that cannot be approximated as "small signal", a requirement that needs to be adhered to in applying the Scher-Montroll theory. The space-charge effects lead to two distinct features in the transients:

(1) "flattening" of the part of the transient before the apparent transit time
(2) additional broadening of the distribution of arrival times of the carriers at the counter electrode due to the effect of slowing down the carriers that are left close to the injecting electrode and thus remain in lower electric field.

Strong dependence of the carrier mobility on field and temperature indicate Poole Frenkel-like activated hopping transport. A thickness dependence stronger than that suggested by the Scher-Montroll theory is found. Significant enhancement of the effective carrier mobility is noticed with the increase of nanoparticle concentration, still well below the percolation limit. This behavior is modeled assuming the encounter of a carrier with a nanoparticle results in the loss of the "memory" that carrier possesses in dispersive (non-Markoffian) transport. Due to the large potential difference across a nanoparticle, considerable acceleration of a carrier is possible due the mobility of holes in the semiconductor being much higher that that of the polymer matrix. At present, it is difficult determine what degree of scattering will be present in CdS nanoparticles (that is to what degree the movement of the carrier inside the nanoparticle can be of ballistic character), but it likely that at least some of the carriers may be ejected from nanoparticles with sufficient initial velocity to be considered entering the dispersive transport anew. This is illustrated Figure 1. Figure 2 shows a comparison of the experimental dependences of the effective mobility on the concentration of nanoparticles with a simplistic model in which the mobility of the composite is calculated as an "effective mean-free-path" dependent quantity.
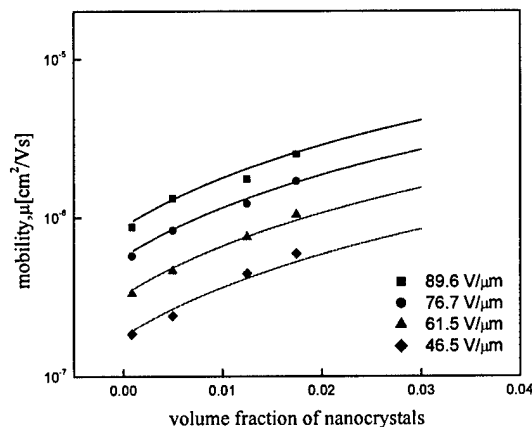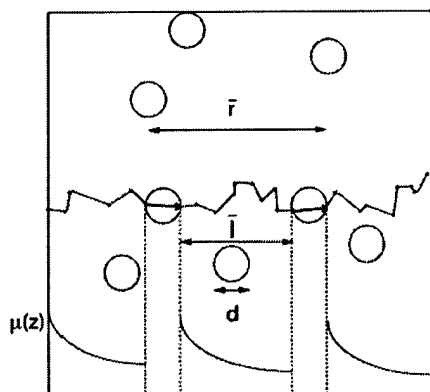

volume fraction of nanocrystals

Figure 1. A scheme of transport of charge carriers through the nanocomposite

Figure 2. Dependence of the hole mobility on varying concentration of nanoparticles at four different applied electric fields. The solid lines are theoretical fits to the data.

9. K. RoyChoudhury, M. Samoc, A. Patra and P.N. Prasad, J. Phys. Chem. B 108, 1556-1562 (2004).